MULTIELEMENTAL ANALYSIS OF DRINKING WATER USING PIXE TECHNIQUE

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ABSTRACT

Non-destructive proton induced X-ray emission (PIXE) in combination with pre-concentration technique was used for the analysis of trace and toxic elements in drinking water. The pre-concentration technique was applied to increase the analytical sensitivity of the most elements detected by PIXE method and to obtain dry dissolved solids. The mean concentration values of the elements (Al, Ca, Co, Cl, Ti, V, Cr, Mn, Fe, Si, Zn, Br, As, Rb and Sr) in drinking water samples were determined simultaneously at the parts per billion (ppb) levels. The drinking water samples and certified reference materials (CRMs) were irradiated with 2.0 MeV proton beam from Van de Graaff accelerator. The concentration of these elements varied from one city to other depending on the geographical locations where the samples were collected. The results were compared with the published data, Iraqi standards (IRQ), European standards (EU), and World Health Organization (WHO) guidelines for drinking water quality.

KEYWORDS: Pre-Concentration Technique, PIXE Analysis, Multi Elemental Analysis, Drinking Water Quality

INTRODUCTION

In general there are three categories of naturally occurring water resources: river water, surface water and ground water, and as well as rain waters are necessary in our life. In Iraq Tigris and Euphrates rivers are the main source of water supply for drinking, domestic uses, irrigation, generate electric power from hydropower stations and other uses. Discharge of untreated waste from domestic, industrial, hospitals, and agricultural or other human activities to the rivers is increasing the concentration of trace and toxic elements in water every year and this has an effect on the human health for long time of life. The quality of drinking water [1] may be controlled through a combination of protection of water sources, control of treatment process and management of the distribution and handling of the water.

Applications of PIXE [2-5] in combination with pre-concentration technique [2-6] have been used for determination of multi-element concentration levels in tap water [2, 5], drinking water [4] and river water [7]. PIXE technique has the advantages [2-5] of non destructive, multi-elemental analysis, cheaper than other techniques, speed of analysis for a wide variety of samples, simplicity, and adequate, high sensitivity technique. These features of PIXE greatly improve signal to noise ratio [7, 8] of trace elements in spectra and enable to detect much lower levels of concentration [8, 9] in the parts per billion (ppb) ranges. In the present study drinking water were collected from 20 cities across Iraq and analyzed for trace and toxic elements using PIXE with pre-concentration technique. Water samples and U.S. reference material (GSP–2), Granodiorite, Silver Plume, (U. S. Geological Survey reference material) are bombarded with 2.0 MeV protons. Standard reference material (SRM) was used for the analysis of all elements present in the water samples. Present results are compared with the published data [2-6], and as well as WHO-1996 [10], Iraqi standards [11], and European standards [12] guidelines for drinking water quality.

EXPERIMENTAL TECHNIQUE

Water Sample Preparation

Drinking water samples were collected directly from twenty cities across Iraq using clean polyethylene bottles of 2 liters without coming into contact with hands and other materials. Drinking water samples were processed directly in order to minimize losses of trace elements due to the adsorption effects. 5 ml of HNO_3 added to 1 liter of water to prevent the loss and adhesion of the trace elements on container glass walls. The pre-concentration procedure [3, 6] was applied to water samples by evaporation at $50^{o}C$ under atmospheric pressure to obtain dry dissolved solid residue. Total solid concentration is the weight of the residue left after water is evaporated to dryness in (g/L). The weights of the final dissolved solids from one liter of drinking water were in the range of 0.54 – 1.52 g/L and its average value of 0.82 g/L. The final dissolved solids were milled in an agate mortar to homogenize and were pressed into 5 mm diameter and 1 mm thick pellets using a stainless steel hydraulic press.

PIXE Analysis

Elemental analysis by PIXE was performed with 2.0 MeV proton beam from Van de Graff accelerator at the King Saud University, Saudia Arabia, the experimental setup was described by Al-Bedri et al.[13]. Drinking water samples with standard reference materials (GSP-2) were irradiated with 2.0 MeV protons for 20 minutes in a vacuum chamber. A thin layer of 50 µm-thick Kapton funny filter [14, 15] was placed in front of the detector. This allowed an increase in the signal-to-noise ratio of trace elements [16]. Emitted characteristic X-rays induced by proton beam were detected by a Si(Li) detector with an energy resolution of 175 eV (FWHM) at 5.9 keV (Mn K_{α} X-rays) and an active area of 30 mm^2. The output data were analyzed with a standard electronics and a computerized multichannel analyzer. The concentrations of the elemental constituents in the sample were calculated from PIXE spectra using Guelph PIXE (GUPIX) software package [17] and measured by relative method was discussed by Al-Bedri et al. [13] using standard reference materials. The standard reference materials GSP–2 were used to calibrate the system and to measure the accuracy of PIXE procedure. In this study, the standard reference elements used were actually very similar in composition to the drinking water samples analyzed. The present study describes the capability of PIXE technique for monitoring the quality of drinking water in Iraq, and to determine the concentration levels of trace and toxic metals in drinking water.

METHODS OF ANALYSIS OF PIXE SAMPLES

The analysis is performed by first measuring the X–ray yield $A_i\ (E)$ at X-ray energy detected in the peaks of the spectrum by Campbell [18], according to the following equation:

$$A_i\ (E) = N_i\,N_p\,\epsilon_i\ (\Omega\ /4\pi)\ \mu_i\ C_i \int_{E}^{o} \sigma_i\ (E)\ [S_a(E)]^{-1}\ exp\ (-\mu_a x)\ dE \tag{1}$$

where $A_i\ (E)$ = X–ray yield at X–ray energy corresponding to the *ith* element in the sample

N_i = Number of target atoms per unit volume of the element *ith*

N_p = Number of incident protons at the same energy E

ϵ_i = Detector efficiency at X–ray energy corresponding to the element i

Ω = Detector solid angle

μ_i = Absorption coefficient for X–rays of element *ith* in emerging a path length *x* in thick sample

$\sigma_i(E)$ = X–ray production cross section for the element *ith*

$S(E)$ = Stopping power of proton at energy *E* in thick bread sample

dE = Energy loss of protons in thick sample.

If a sample contains more than one atomic component contributing to the stopping power, the total stopping power can be calculated using Bragg – Kleeman rule as given by:

$$S(E) = \sum_i^n C_i S_i(E)$$

(2)

where S *(E)* = the stopping power of the matrix for proton energy *E*

N = Number of the atomic component

$S_i(E)$ = The stopping power of the *ith* element in water sample

C_i = The fraction of the *ith* element in the matrix (= 1 for pure element).

In our case Eq. (1) becomes:

$$A_i(E) = N_i N_p \epsilon_i (\Omega/4\pi) \mu_i C_i \int_E^o \sigma_i(E) [S_a(E)]^{-1} exp(-\mu_a x) dE$$

(3)

Where μ_a refers to the absorption coefficient for the X–rays in the water sample and S_a refers to the absorption stopping power of the water sample. The method in the present work is used to determine the concentration C_i of the *ith* element in the matrix was based on the comparison of X–ray yield $A_{iw}(E)$ from a water sample to that from a standard pure sample $A_{is}(E)$ of the element *ith* when bombarded under the same experimental conditions and with the same number of protons N_p at the same energy *E* and the same geometry. It was felt unnecessary to correct them for geometry, detector efficiency or X – ray absorption after leaving the target. Thus, we have:

$$\frac{A_{iw}}{A_{is}} = C \frac{I_w}{I_s}$$

(4)

Where I_w and I_s are the integral intensity values in Eq. (3) for water sample and standard reference elements respectively. In the above equation *C* refers to the concentration ratio of the trace elements in water sample (C_w) to that in the standard reference (C_s) sample. Since the water sample has the element *ith* as its main constituent, one can assume that the values of the two integrals I_w and I_s will contribute the same i.e. $I_w \approx I_s$ [19, 20]. In this case Eq. (4) will have the form of:

$$\frac{C_w}{C_s} = \frac{A_{iw}}{A_{is}}$$

(5)

RESULTS AND DISCUSSIONS

It is clear that the detector resolution of 175 eV FWHM was quite adequate to resolve X–ray lines for all elements studies in water samples. Equation (5) was employed to determine the elemental concentration in drinking water samples.

In this study, the accuracy of the measurements was checked using GSP–2 standard reference materials (SRMs). Table 1 gives the mean values in µg/g of the elemental concentrations with their standard deviation (S.D.) detected in SRMs compared with the certified values reported by U.S. Geological Survey reference materials. The accuracy of PIXE technique was checked using US standard reference materials GSP–2, Granodiorite, Silver Plume, (U. S. Geological Survey reference material). The agreement between our experimental results and the certified values is within ±0.51% to ±7.69%.

**Table 1: The Mean Concentrations of the Multielements Measured in Standard
Reference Materials (GSP–2) Compared with Certified Values Reported
by U. S. Geological Survey Reference Materials Used for PIXE Procedure**

Element	Measured Value Mean ± S.D. (µg/g)	Certified Value ± S.D. (µg/g)	Accuracy (%)
Al*	8.01 ± 0.10	7.88 ± 0.11	+ 1.65
Ca*	1.60 ± 0.05	1.53 ± 0.04	+ 4.58
Fe*$_{tot}$	3.35 ± 0.15	3.43 ± 0.11	− 2.33
K*	4.60 ± 0.20	4.48 ± 0.12	+ 2.67
Mg*	0.56 ± 0.02	0.58 ± 0.02	− 3.45
Na*	2.10 ± 0.15	2.06 ± 0.07	+ 1.94
P*	0.12 ± 0.01	0.13 ± 0.01	− 7.69
Si*	31.30 ± 0.45	31.1 ± 0.4	+ 6.43
Ti*	0.38 ± 0.01	0.40 ±0.01	− 5.00
Ba	1366 ± 55	1340 ± 44	+ 2.61
Co	7.45 ± 0.65	7.3 ± 0.8	+ 2.05
Cr	21.020 ± 6	20 ± 6	+0.51
Cu	45.12±4	43 ± 4	+ 4.93
Mn	322± 15	320 ± 20	+ 0.63
Pb	44.80 ± 2.25	42 ± 3	+ 6.67
Rb	255 ± 8	245 ± 7	+ 6.25
Sr	258 ± 13	240 ± 10	+ 7.50
V	53.10 ± 4.8	52 ± 4	+ 2.30
Zn	126 ± 12	120 ± 10	+ 4.17

* = Wt%

S.D. = Standard deviation

In general, the weights of the final dissolved solids of all inorganic and organic elements from one liter of drinking water were in the range of 0.54 – 1.52 g/L with its average value of 0.82 g/L are relatively lower than the guideline values [1, 10, and 12]. This low elemental concentration contents makes drinking water ideal for drinking after treatment. Tables 2 represents the range and mean concentration results ± standard deviation (S.D.) in µg/L for all elements (Al, Ca, Co, Cl, Ti, V, Cr, Mn, Fe, Si, Zn, Br, As, Rb and Sr) detected in drinking water collected from 20 cities in Iraq. The mean concentration values for the most elements (Al, Ca, Co, Cl, Ti, V, Cr, Mn, Fe, Si, Zn, Br, As, Rb and Sr) detected in drinking water are varied from one city to other which are in agreement with data published by Al-Bedri *et al.* [6] for Euphrates and Tigris rivers water and a similar observation was reported by Ndiokwere *et al.* [21]. This variation in the concentrations of the detected elements in the drinking water may be due to the geographical locations and the local contamination of Euphrates and Tigris rivers which flows through a large number of industrial cities in Turkey, Syria and Iraq.

The present values of the elemental concentrations in drinking water were found in agreement with the data published by Yamazaki et al., 1996 and Yamazaki et al., 2002 for drinking water, and were lower than the results reported

by Amartaivan et al., 2002 and Al-Bedri et al., 1991 for river water, and as well as Iraqi standards [11], WHO [10] guideline values for drinking water quality, EU standards [12].

**Table 2: Range and Mean Concentration in µg/L of Trace
and Toxic Elements in Drinking Water Using PIXE Technique**

Element	Range (µg/L)	Mean ± S.D. (µg/L)
Al*	0.02 – 5.2	0.25 ± 0.12
Ca*	19.5 – 235.59	124.05 ± 55.20
Co	0.44 − 3.02	2.25 ± 0.42
Cl	0.41 – 14.82	5.01 ± 2.34
Ti	0.20 − 0.90	0.49 ± 0.16
V	0.75 – 4.12	1.58 ± 0.42
Cr	0.35 – 4.92	1.64 ± 1.01
Mn	0.15 – 15.4	6.10 ± 3.21
Fe	33.00 – 1460	230.20 ± 85.20
Si*	1.09 – 18.12	3.30 ± 2.22
Zn	12.01 – 1590	220.22 ± 98.20
Br	0.11– 30.20	3.92 ± 1.25
As	1.11 – 6.45	2.252 ± 1.24
Rb	0.92 – 4.33	2.52 ± 0.98
Sr	0.24 – 2.80	1.02 ± 0.62

* = mg/L

CONCLUSIONS

The present work deals with chemical analysis of the drinking water samples collected from twenty cities across Iraq focusing on the determination of trace and toxic elements contents (Al, Ca, Co, Cl, Ti, V, Cr, Mn, Fe, Si, Zn, Br, As, Rb and Sr) by means of PIXE technique. Non-destructive PIXE technique, used with pre-concentrated water, leads to improve the sensitivity below the ppb level and describes the capability of PIXE technique for monitoring the quality of drinking water. The concentrations of the elements detected in drinking water were lower than the limits of the Iraqi standards, European standards and WHO guidelines values for drinking water quality.

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